

# Clay swelling inhibition mechanism of $\alpha,\omega$ -diaminoalkanes in Portland Brownstone

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Many clay-bearing sedimentary stones such as Portland Brownstone will swell when exposed to water, and this can generate damaging stresses as differential strains evolve during a wetting cycle. Current swelling inhibitors, consisting of  $\alpha,\omega$ -diaminoalkanes, can reduce swelling in Portland Brownstone up to 50%. In this study, through x-ray diffraction and swelling strain experiments, we demonstrate that the  $\alpha,\omega$ -diaminoalkanes inhibit swelling by substituting for interlayer cations and partially hydrophobicizing the interlayer, then rehydrating on subsequent wetting cycles. We also introduce the copper (II) ethylenediamine complex as a potential treatment for swelling inhibition.

## I. INTRODUCTION

Portland Brownstone, a sandstone widely used throughout the northeastern United States in historic buildings and monuments, shows damage that is related to the swelling of clay in the stone. These clays cause differential stresses and strains that lead to buckling and cracking, and the clays may also create small pores that make the stone susceptible to damage by salt crystallization or frost.<sup>1</sup> As the exterior surface of the stone absorbs water, the wet layer expands with a strain  $\epsilon_s$  relative to the dry interior, which creates a compressive stress,  $\sigma_x$ , parallel to the surface in the wet layer. This is strictly analogous to the compressive stress created when the surface of a plate is heated<sup>2</sup>; the stress in a stone when the surface experiences hygric swelling is presented by González et al.<sup>3</sup> When that layer is thin compared with the dry interior, the stress is<sup>3,4</sup>

$$\sigma_x = \frac{E_w \epsilon_s}{1 - \nu_w},$$

where  $E_w$  is the elastic modulus of the wet stone (which may be much less than that of the dry stone<sup>5</sup>), and  $\nu_w$  is Poisson's ratio. If a treatment is applied that reduces  $\epsilon_s$ , without increasing  $E_w$ , then the stress is reduced.

Most of the damage observed is of the buckling type (as seen in Fig. 1), where large surfaces buckle away from the surface during wetting, although exposed

elements can crack upon drying.<sup>3</sup> The buckling mechanism is discussed elsewhere.<sup>6</sup> Briefly, it is known that buckling from compressive stress is possible in plates only if their width-to-thickness ratio is large,<sup>7</sup> but if the wetting is inhomogeneous, the swelling pattern can cause local bending moments<sup>8</sup> that put stress on small defects. Finite element simulations show that these stresses are large enough to cause growth of existing defects, which could lead them to coalesce into large enough defects to allow buckling.<sup>9</sup> It has been demonstrated that treatment with surfactants can reduce swelling,<sup>10–13</sup> so it is expected to improve the longevity of buildings made of such stones. In this paper, we show the mechanism of strain suppression by  $\alpha,\omega$ -diaminoalkane surfactants through tests on pure clays and whole stone.

It is common to find swelling clays in sedimentary stones, and these clays can lead to many engineering problems in the fields of tunneling, oil well borehole stability, and foundation stability.<sup>14–16</sup> It was recognized as a problem in conservation by Delgado,<sup>17</sup> and others have contributed to the study of this problem more recently.<sup>18</sup> Wendler and Snethlage devised and tested an  $\alpha,\omega$ -diaminoalkane treatment that was found to be effective on some swelling German sandstones and on swelling stones on Easter Island.<sup>10,11</sup> This treatment consisted of a linear hydrophobic alkane chain with protonated amine groups at each end; the amines are believed to substitute for the alkali in the interlayer of the clay and act to bind opposing sheets together, while the hydrophobic chain discourages water entry. González and Scherer tested and found this treatment to be effective on Portland Brownstone and also found that there is sensitivity to the order of addition of these

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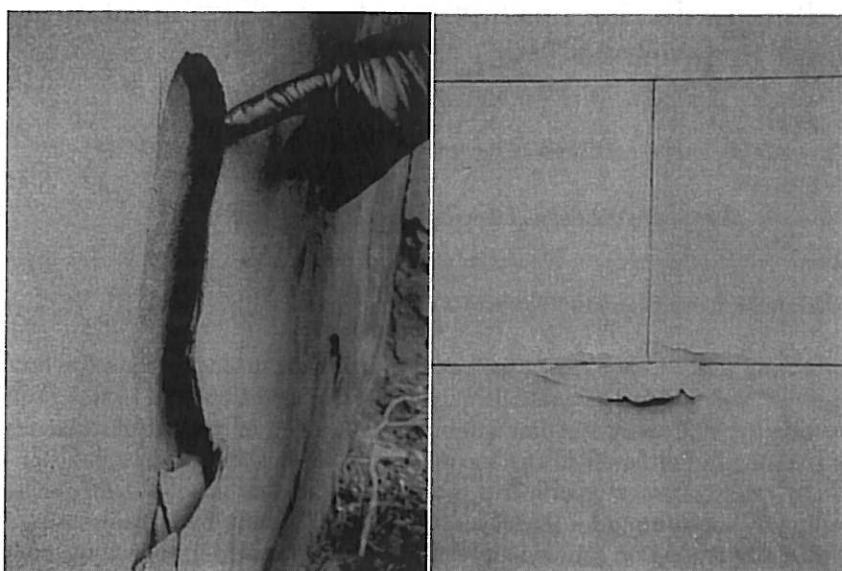


FIG. 1. Examples of buckling damage as seen on the Victoria Mansion (Portland, ME), a 19th century building constructed with Portland Brownstone.

surfactants, and that mixtures of surfactants could be a more effective treatment<sup>12</sup>; these observations were confirmed by Wangler et al.<sup>13</sup> Another advantage of swelling inhibitors is that they improve the performance of silicate consolidants,<sup>19,20</sup> which otherwise fail after one or two wetting cycles.<sup>21,22</sup> Gonzalez and Scherer also found that, because the clay is in the cementing phase of the stone, it has a large effect on the elastic and viscoelastic properties.<sup>12</sup> They found that the diaminoalkane (DAA) treatment raised the modulus of the stone while increasing the viscoelastic relaxation rate, so any immediate reduction in swelling from the treatment may be offset by an increase in the modulus, although the stress may relax away faster. The DAA treatment has also been found to be quite stable with respect to washout,<sup>23</sup> but all attempts at optimizing it have been unsuccessful at fully eliminating swelling.<sup>12,13</sup> The goal of the present study is to understand the mechanism by which the DAA reduces swelling, with the idea that this knowledge can be used to further optimize the treatment or potentially reveal other options. Most evidence<sup>10-13</sup> seems to indicate that swelling is reduced by intercalation of the DAA in the interlayer via ion exchange. The effect on the mechanical properties indicates that intercalation is taking place, and the resistance to washout indicates that ion exchange is taking place rather than complexation of the amine to the cation or the negatively charged clay surface of the clay interlayer. However, the source of the residual swelling has been a mystery. A recent study proves that Portland Brownstone swells almost entirely by intracrystalline swelling,<sup>24</sup> with no significant contribution from osmotic effects, so it is possible that the DAA in the interlayer are still hydrating upon wetting.

There is too little clay in Portland Brownstone for direct study of the stone by x-ray diffraction (XRD). Therefore, we examine clays separated from the stone, as well as a high-swelling clay, sodium montmorillonite, during wetting and drying, with and without exposure to DAA. Of course, neat clays exhibit much larger strains than clay confined between the grains in a stone, where the network of rigid grain contacts exerts a confining stress on those grain boundaries containing clay. It is clear that some grain contacts contain clay, because the elastic modulus of Portland Brownstone decreases strongly ( $\sim 50\%$ ) when the stone is wet; however, the modulus does not drop to zero, so many of the grain contacts must be relatively free of clays (as indicated schematically in Fig. 2). The network of relatively rigid clay-poor grain boundaries acts like a spring that resists the expansion of the clay-rich boundaries, so the clay is subjected to compression as it tries to swell.

## II. EXPERIMENT

### A. Materials

The materials studied in these experiments were laboratory-grade bentonite powder (primarily Na-montmorillonite, obtained from Fisher Scientific) as the neat clay and Portland Brownstone (from Pasvalco Corp., Closter, NJ) for the stone studies. Chemicals were obtained from Acros Organics and included  $\alpha,\omega$ -diaminoalkanes (DAA) with carbon chain lengths of 2, 3, 4, 6, and 8. Also obtained were hexamethonium bromide, an  $\alpha,\omega$ -diquaternaryammonium alkane with a carbon chain length of 6, and a copper (II) ethylenediamine complex solution.

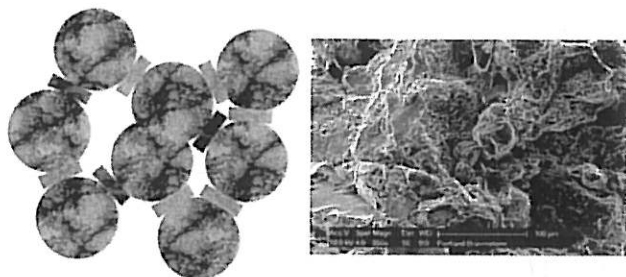


FIG. 2. As seen in the schematic, the cementing material at some grain boundaries is rich in clay (darker), while other boundaries are relatively free of clay (lighter); the latter remain rigid during wetting, and form a network that constrains the expansion of the clays. The scanning electron micrograph shows the microstructure of the stone, with clays of the cementing phase coating the quartz and feldspar grains.

### B. Clay separation

For separation of the clay-sized fraction from the stone, a procedure adapted from USGS Open File Report 01-041 was used.<sup>25</sup> It consisted of manually grinding a few hundred grams of stone with a mortar and pestle and then performing a series of sonication, sedimentation (settling time determined by Stokes settling), and decantation cycles until the decanted portion was visually clear. A dispersant (Calgon) was added to the mixtures, and because there is little to no calcite content, no acid pretreatments were necessary.

### C. X-ray diffraction studies

X-ray diffraction studies were performed on a Rigaku Miniflex (Cu K $\alpha$ ) diffractometer (The Woodlands, TX). Samples were prepared for XRD studies by drying several milliliters of clay suspension (either bentonite or separated clay fraction from Portland Brownstone) on a glass slide to obtain preferred orientation along the basal planes. Scans were performed of the expected 001 basal spacing region, from about 4 to 12° 2 $\theta$ . Treatments on clays were performed by direct application of the 0.31 M diaminoalkane solution to the oriented clay on the slide followed by drying. Scans were performed under dry and wet condition; for wet conditions, samples had water applied and were observed before and after the experiment to ensure some water was still present in the sample.

### D. Treatment procedure

The treatment procedure for stone samples followed that of previous studies.<sup>12,13</sup> Samples (roughly 5 × 5 × 45 mm) were soaked in a solution of a particular concentration of treatment for 1 to 3 h to ensure full saturation, dried at ambient for approximately 1 h, and then placed in a 60 °C oven overnight. Most treatments were performed at 0.31 M in total diaminoalkane concentration, corresponding to the diaminoalkane concentration of 5 wt% diaminobutane used by Wendler in the initial studies of this treatment.

### E. Swelling experiments

Swelling experiments were performed with a linear variable differential transformer (resolution ~0.2  $\mu$ m) obtained from Macrosensors (Pennsauken, NJ) monitoring the displacement of the sample in a flat-bottomed cup after swelling fluid was added. The experiment was allowed to proceed until saturation was complete, which was about 15 to 30 min. Samples were always measured after coming out of a 60 °C oven and equilibrating with ambient temperature while sealed in a closed container (to avoid atmospheric moisture). In some experiments, a nitrogen flow was added above the cup to speed the drying.

## III. RESULTS

### A. XRD

The XRD experiments performed on neat bentonite demonstrate a shift in the d-spacing between untreated wet and dry samples, indicating intercalation by water. Most diaminoalkanes increased the basal spacing to about 13 Å. Ethylenediamine had a smaller basal spacing, probably owing to the smaller size of the molecule. Under wet conditions, peak shifts were observed for the untreated, ethylenediamine-treated, and diaminopropane-treated clays. The diaminobutane and diaminohexane treated samples did not show any shift under the wet conditions of this experiment. Figure 3 shows the XRD scans. An experiment was run in which a lower concentration (~0.08 M) of diaminobutane treatment was applied to the clay. Figure 4 is the diffractogram of that experiment, showing a sharp peak at about 16 Å under wet conditions.

Figure 5 shows the diffractogram for the separated clay fraction of Portland Brownstone. Peaks are seen for chlorite, illite, and possibly kaolinite (all non-swelling clays) and there is no peak shift when wetted or glycolated. The 14 Å peak does not collapse after heating to 550 °C, indicating that it is not a vermiculite peak.<sup>25</sup> The absence of a peak shift after glycolation is disconcerting at first; however the previously cited study<sup>24</sup> confirms the existence of intracrystalline swelling in clay layers via experiment with organic solvents and cation substitution. This implies the existence of randomly interstratified swelling layers throughout the chlorite fraction.

### B. Swelling experiments

Standard swelling experiments were performed to characterize the untreated swelling of Portland Brownstone, and it was found to be  $1.0 \pm 0.05$  mm/m. (Examination of a wide variety of Portland Brownstone samples in our lab yields swelling strains ranging from about 4 to  $10 \times 10^{-4}$ , so the present sample is at the upper end of the range for this stone.) A series of experiments was

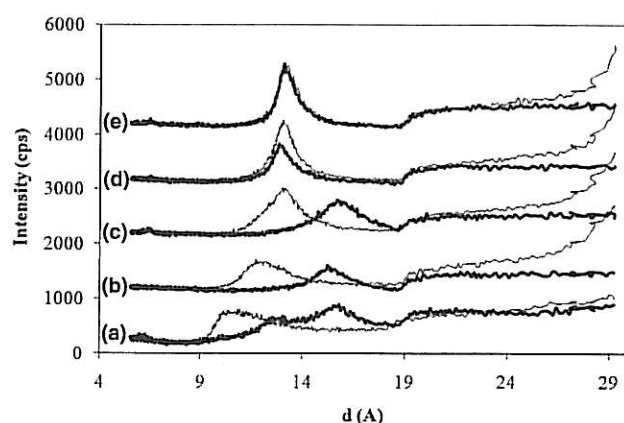


FIG. 3. Diffraction patterns (Intensity,  $I$ , in counts per second, versus  $d$ -spacing, curve A is baseline and all others progressively offset by 1000) of bentonite clay peaks under wet and dry conditions and with various diaminoalkane treatments. Darker lines are wet scans. Curves are labeled: (a) untreated, (b) ethylenediamine (C2), (c) diaminopropane (C3), (d) diaminobutane (C4), and (e) diaminohexane (C6).

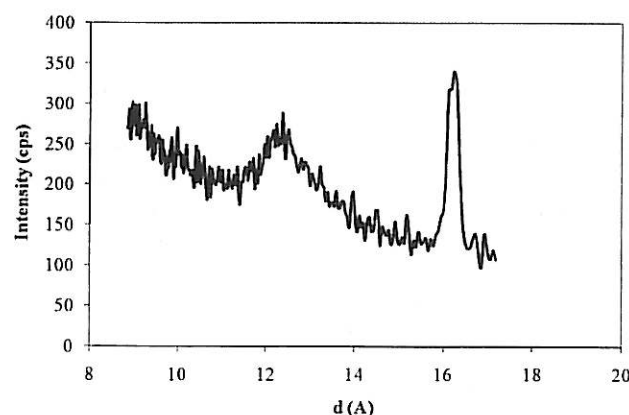


FIG. 4. Diffraction pattern (Intensity in counts per second versus  $d$ -spacing in Å) of Na-montmorillonite treated with low concentration (0.08 M) of diaminobutane. Sharp peak at about 16 Å confirms existence of double layer hydrate for larger diaminoalkane.

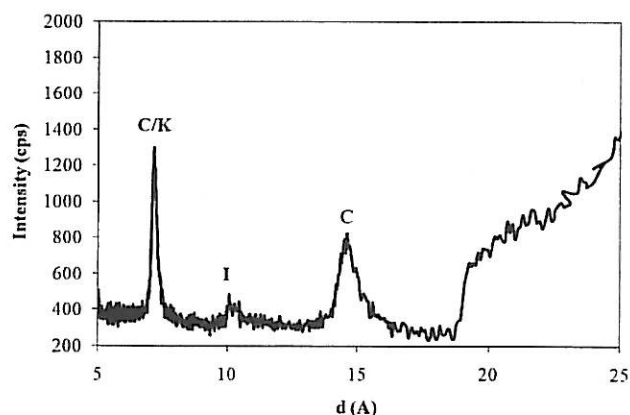


FIG. 5. Diffraction pattern (intensity in counts per second versus  $d$ -spacing in Å) of Portland Brownstone oriented clay fraction. Chlorite, illite, and chlorite/kaolinite peaks are marked. No peak shift was observed upon glycolation.

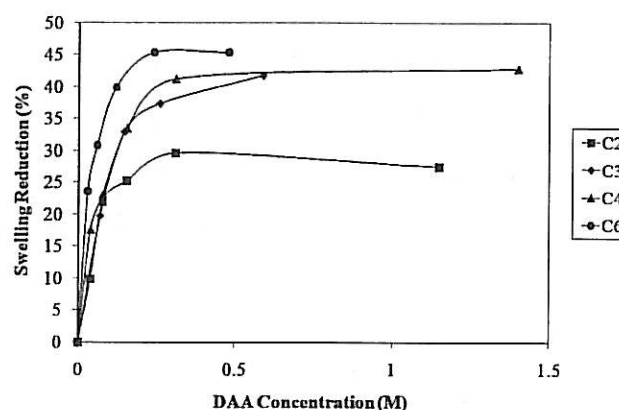


FIG. 6. Swelling reduction versus diaminoalkane treatment concentration. Each curve corresponds to an  $\alpha,\omega$ -diaminoalkane with the indicated carbon chain length.

then performed to see the effect of concentration of DAA treatment on the swelling reduction. The results shown in Fig. 6 indicate a ceiling of about 40 to 50% reduction of the swelling. Since it is believed that the DAA substitute for random charge sites in the interlayer, it was hypothesized that a mixture of varying chain lengths would be more effective. A solution of equimolar concentration of DAA (total DAA concentration = 0.31 M) utilizing carbon chain lengths of 2, 3, 4, 6, and 8 was tested and the swelling reduction was 50%, making it the most effective single DAA treatment performed, but still having a residual swelling strain. Finally, because it was shown<sup>24</sup> that almost all the swelling in Portland Brownstone is intracrystalline, and since organometallic complexes are known to bind strongly in the interlayer space,<sup>26</sup> the copper (II) ethylenediamine complex was tested for its effect on swelling. It showed a 70% reduction in swelling for the duration of this experiment, making it the most effective swelling inhibitor in Portland Brownstone to date.

### C. Swelling/drying/rewetting treatment experiments

These experiments consisted of monitoring the displacement of a stone sample throughout an entire treatment cycle. The treatment was directly applied, then excess liquid was removed with a syringe; the sample was dried with nitrogen, and then rewetted with water. Three treatments were tested with this experiment: the 0.31 M solution of DAA mentioned previously, 0.31 M diaminohexane, and (to differentiate the amine chemistry's effects on the treatment mechanism) 0.31 M hexamethonium bromide. The results of these three experiments are shown in Figs. 7(a)–7(c). The important features are: (i) all curves swell to approximately 70% of the full water swelling strain, (ii) additional swelling does not occur (in fact, sometimes



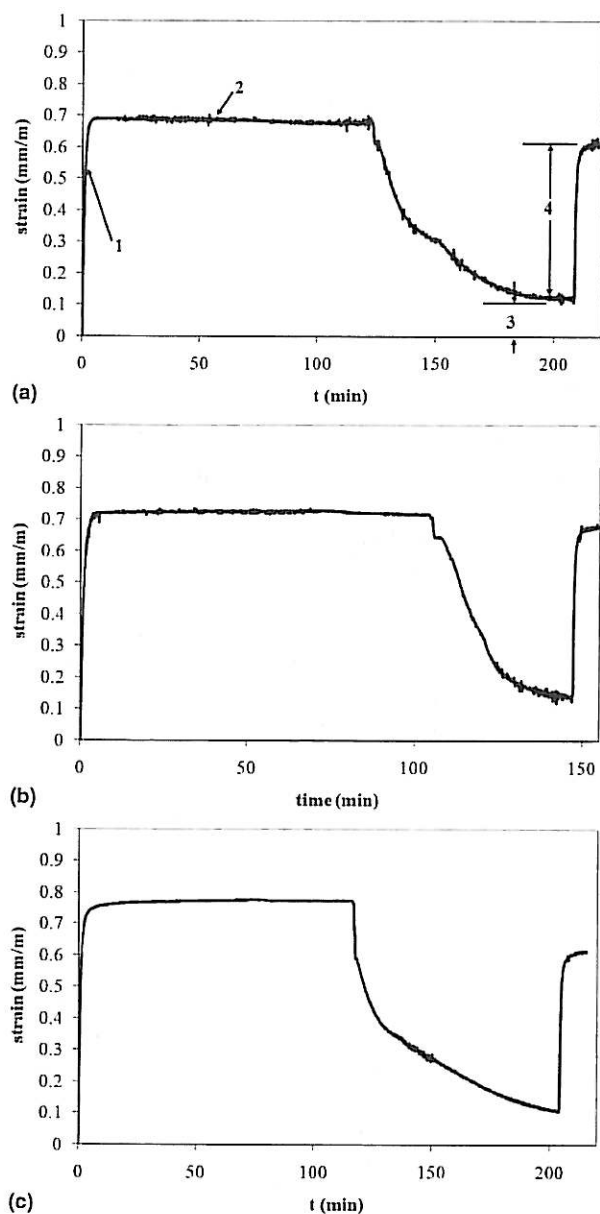


FIG. 7. Direct treatment swelling/drying/rewetting curves for (a) 0.31 M diaminoalkane solution, (b) 0.31 M diaminohexane, and (c) 0.31 M hexamethonium bromide. Kinks in drying curves are due to details in the drying process for individual samples. Common curve features are marked in (a): (1) swelling with treatment does not proceed to untreated swelling level of 1.0 mm/m, (2) swelling remains restricted or decreases during exposure to treatment, (3) residual "intercalation" strain, and (4) posttreatment swelling strain with water. The posttreatment swelling strain was verified with an additional oven-dried swelling strain experiment. Actual swelling reduction is equal to the original swelling strain minus the sum of the posttreatment swelling strain and the "intercalation" strain.

slight reduction occurs) during extended exposure to the treatment, (iii) drying reduces the strain to near the baseline level, but not completely, and (iv) subsequent rewetting shows the "treated" swelling strain rising to a level lower

than the initial "treatment" swelling strain. It was not possible to heat the sample during the experiment, but the final swelling strain was remeasured after oven drying the treated sample at 60 °C and the swelling was unchanged.

#### IV. DISCUSSION

A separate study<sup>24</sup> found that almost all the swelling in Portland Brownstone is intracrystalline swelling, corresponding to about four pseudomonolayers of water and with no significant contribution from osmotic effects. This conclusion was based on the swelling observed in samples pretreated with solutions of cations that form inner-sphere hydrates, as well as a series of organic liquids. An increase in clay layer spacing produces a proportional increase in stone dimension: for Portland Brownstone, a 1 Å increase in layer spacing corresponds to approximately 0.11 mm/m increase in strain. Moreover, swelling typically begins from a completely dehydrated state, or a basal layer spacing of about 10 Å. This information is essential in the evaluation of the diaminoalkane treatment mechanism.

The results of XRD studies on the separated clay fraction of Portland Brownstone highlight the potential difficulties encountered in studies of this sort on the clays from stones. All the clay peaks in Portland Brownstone are nonswelling clay peaks, as evidenced by the lack of peak movement upon glycolation. It has already been demonstrated that intracrystalline swelling is responsible for almost all swelling observed in Portland Brownstone,<sup>24</sup> so it can reasonably be assumed that the swelling clay layers are randomly distributed throughout the chlorite clay fraction, as it is known that chlorites can weather into swelling clays.<sup>27</sup> XRD studies on Na montmorillonite served as a model system, and they demonstrated that intercalation takes place and increases the basal spacing by 2 to 3 Å. However, the most interesting result from the XRD experiments is the fact that the DAA demonstrate that they can hydrate upon wetting, although only the shorter chain length DAA did so at the normal treatment concentration. The fact that both short-chain DAA hydrated to a basal spacing of approximately two pseudomonolayers of water (~15 to 16 Å) is significant. All studies of DAA swelling reduction in stone indicate a ceiling of 50% reduction,<sup>12,13</sup> which would correspond to two pseudomonolayers of water. A major inconsistency, however, is that the larger chain length DAA did not show the double-layer hydrate in the neat clay, although from all indications in the stone swelling experiments, it exists. We suspected that the neat clay could take up enough DAA to become hydrophobic, whereas the confined clay in the stone could not. Therefore, we tested the expansion of neat clay exposed to a lower concentration of DAA. When the diaminobutane treatment solution was diluted by about 4×, a sharp

peak corresponding to the double-layer hydrate did appear under wet conditions. This supports the idea that the diaminoalkane molecules are hydrating in the stone clay layers (however, we cannot exclude the possibility that the negatively charged clay layer itself is hydrating).

The results of the concentration versus swelling reduction studies for various diaminoalkanes verify the ceiling to swelling reduction achievable with this treatment, as most treatments reduced swelling up to about 40 to 50%. The fact that the solution mixture of varying chain lengths was the most effective single treatment indicates that a mixture of chain lengths is more efficient at fully exchanging the randomly situated charge sites in the interlayer. The experiments that are the most useful in understanding the treatment mechanism are the direct treatment/drying/rewetting experiments. The initial rise of each curve is  $\sim 25$ – $30\%$  lower than the full, untreated, water swelling strain. This is an indication that the DAA are entering the interlayer immediately, although the full exchange does not necessarily have to occur instantaneously. Indeed, the fact that the swelling curve remains constant, and in some cases begins to decrease, throughout the exposure to the treatment indicates that the exchange/intercalation is occurring. It may be that the limit to treatment time is not necessarily the saturation time of the stone's porosity, but is controlled by the diffusion of DAA into the interlayer of clay particles and subsequent displacement of the cations currently residing there. Drying the sample reduces the strain to a level that is above the original dimension of the sample, indicating that intercalation has taken place and the molecules are propping open the layers. However, using the results of the neat clay XRD studies (showing an intercalation basal spacing increase of about  $3 \text{ \AA}$ ) along with the scaling factor of  $0.11 \text{ mm/m-\AA}$ , one would expect to see a residual "intercalation" strain of  $0.33 \text{ mm/m}$ , and the observed strain is much lower than that in these experiments. This is an indication that, although intercalation is occurring, the clay layers are collapsing around the diaminoalkanes. In fact, the neat clay XRD studies may be deceptive because they are not performed under pressure, and in the case of the stone the surrounding stone matrix applies pressure to the clay layer and pushes the clay layers down around the intercalating DAA molecules. The final swelling strains upon rewetting agree with the swelling reductions that we observe, so the actual swelling reduction is equal to the difference between the full swelling strain ( $1.0 \text{ mm/m}$ ) and the top of the rewetting curve (or, the total swelling strain minus the sum of the rewetting strain and the residual "intercalation" strain)—approximately 30 to 40%. The degree of collapse, or the magnitude of the "intercalation" strain, is probably the reason that ethylenediamine's ceiling to swelling reduction was much lower than all other DAA—the shorter chain length DAA probably allows

the layers to collapse more readily around it. The "treated" swelling strain is restricted (in contrast to swelling behavior with monofunctional amines and quaternary ammonium ions) likely because in some cases, opposite ends of the difunctional molecule are balancing charges on opposite layers, just as Wendler hypothesized.<sup>10</sup> The DAA molecules are lying flat in the interlayer, and some of them must have opposing ends "keyed" into opposite sheets. Lastly, the similar behavior of hexamethonium bromide to diaminoethane is a final verification of the mechanism of ion exchange for the DAA, as hexamethonium bromide is unable to form amine complexes with the interlayer cations or negatively charged clay surfaces.

It should be noted that for all of these experiments, the degree of exchange is unknown. It is possible that if incomplete exchange is occurring, the residual "intercalation" strain could increase without increasing the magnitude of the final rewetting swelling curve. This would act to increase the apparent swelling reduction. All indications are, however, that complete exchange is occurring, as very high concentrations of DAA ( $>1 \text{ M}$ ) produce the same results. (These high concentrations of DAA are unrealistic as treatments for monuments, because high concentrations can alter the appearance of the stone.) In light of the neat clay XRD results, it may still be possible to achieve complete hydrophobicization of the interlayer, although this may be dependent on some factors that differ between the neat clay and the Portland Brownstone swelling clay, such as interlayer charge density and location.

Given this ceiling to the effectiveness of the DAA treatment, it was supposed that an organometallic complex, such as the copper (II) ethylenediamine complex, could suppress swelling more effectively. The complex is strongly bound and in fact has been suggested as an alternative for use in cation-exchange capacity experiments.<sup>28</sup> The complex consists of a copper cation surrounded by two bidentate ethylenediamine ligands. The ligands could act as a hydrophobic "shell" around the cation, lowering the hydration energy. The complex is the best performing Portland Brownstone swelling suppressor to date, at least for the duration of the swelling experiment ( $\sim 0.5$  to  $1 \text{ h}$ ). It still allows swelling, however, so its effect on the mechanical properties must still be tested. The same reasoning applies to the potential use of hexamethonium bromide as a treatment—if there is no increase in the modulus, it may be a viable candidate for treatment of monuments.

## V. CONCLUSIONS

The diaminoalkane molecules are either partially or fully exchanging and intercalating into the interlayer via an ion exchange reaction; the clay layers are collapsing to a certain degree around the intercalant, and then

rewetting produces subsequent hydration to a double-layer hydrate that is restricted from further increase by the difunctionality of the diaminoalkane molecule. This places a ceiling of about 50% reduction on the effectiveness of the treatment in Portland Brownstone. There still exists the possibility that full exchange has not occurred, or possibly that a higher chain length diaminoalkane or polyamine will be able to completely hydrophobize the interlayer. Organometallic complexes may be more effective at making the interlayer hydrophobic, as the copper (II) ethylenediamine complex seems to be. Another organometallic complex may be more effective, or possibly a mixture of any of these treatments may ultimately prove the best. Whatever the case, unless a treatment completely eliminates swelling, the effect on the modulus must always be tested.

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